

FIXATION OF ATMOSPHERIC NITROGEN

BY

A. T. R. WEATHERS

ARMOUR INSTITUTE OF TECHNOLOGY

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The fixation of atmospheric
nitrogen



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THE FIXATION OF ATMOSPHERIC NITROGEN

A THESIS

PRESENTED BY

ARMADA T. R. WEATHERS

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 29, 1919

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A. McCormack
Professor of Chemical Engineering

H. M. ...
Dean of Engineering Studies

Dean of Cultural Studies

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Introduction.

The two chief sources of the worlds supply of nitrogen are the Chilean nitre fields and the ammonia compounds from the Mond process in the destructive distillation of coal. The latter source may increase rapidly from its present production of 1,500,000 tons per year because of a larger demand for coke due to the increasing smoke prevention laws. The Chilean export in 1830 was about 1,000 tons. In 1918 it reached the maximum of 3,250,000 tons because of the greater needs because of the war. Geologists have figured that the nitre fields will be exhausted in a decade. The chemical industries require large quantities in the manufacture of nitric acid and ammonia. A much greater quantity is used as fertilizer. Most plants are unable to absorb the free inert molecular nitrogen of the atmosphere but can utilize it from such compounds as nitrates and ammonia. With the increased worlds population and thereby a larger demand for food supplies, a cheap



Introduction.

and more abundant production must be made and with the gradual exhaustion of the nitre fields, other ways must be devised to meet this emergency than the two mentioned.

The atmosphere contains 20 per cent oxygen 79 of nitrogen by volume and small amounts of other gases. It is estimated that every square mile of the earths surface supports 20,000,000 and the entire atmosphere contains about \$ 4-000,000,000,000 tons of nitrogen. So we have unlimited quantities of the gas but in the form where it is most inactive and unavailable. It remains for the present scientists to bring this source to the commercial world.

The history of nitrogen fixation covers almost a century of failures. In the year of 18-30 L.Thompson wrote a paper on the manufacture of Prussian blue from the nitrogen of the air. He used two parts of potash,two of pearlash, one of iron turnings, ground the mass to a coarse powder and heated it in iron pots to a



Introduction.

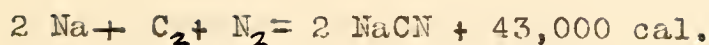
red heat. Berzelius, Bunsen and other chemists who repeated Thompsons experiment failed to get his results. They knew that iron was not necessary to the reaction, left it out and said that Thompson had not fixed nitrogen but admitted it could be done that way. The iron turnings acted as a catalytic agent and Thompson should be given the credit for the first commercial fixation of nitrogen. In 1843 Newton took out patents on this process, He produced 1 ton of potassium cyanide every 24 hours. Newton failed to mix iron with his charges, used refractory retorts and therefore found it necessary to raise the temperature to a white heat disintegrating the retorts with the super heated alkali. The process failed completely and resulted in a great loss of money. In 1881 Victor Alder of Vienna took out patents on the Continent for the manufacture of cyanides by heating carbonates to redness with finely divided iron but stated that iron was not es-

Introduction.

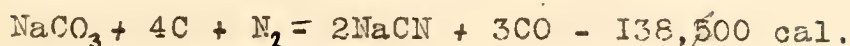
essential to the reaction. In his second series of patents he stated that carbon monoxide or some metal that would carry carbon must be present. All attempts for successful manufacture under these patents proved failures. In 1897 Castner tried cyanide manufacture in the United States with unprofitable results. Whether fixation can be carried on this way is still a question. The chemical Engineers seemed to have abandoned this line and with the large installation of hydro-electric plants all developments have proceeded along electrical methods. A 500,000 horse-power plant has recently been built on the Tennessee River for fixation processes. The fixation processes used commercially may be placed under five distinct lines of development.

- I. The production of cyanides by using alkali metals or carbonates in the presence of iron. The sodium reaction is

Introduction.

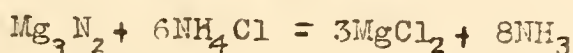
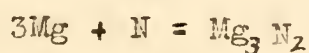
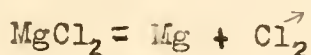


The carbonate reaction is



II. The formation of nitric acid from the atmosphere by the electric arc. Air is heated to the temperature at which nitrogen combines with oxygen to form nitric oxide. The reaction will be given in the article on the chemistry of the process.

III. Methods of heating metallic oxides in an electric furnace to form cyanamids or nitrides as CaCN_2 , CaN , AlN , and MgN .³² The magnesium nitride method may be used in connection with the soda works producing ammonia as a by product. It requires electric current but would recover all the waste sodium chloride and utilize all the unused nitrogen. The reactions are





Introduction.

IV. Processes producing ammonia directly from nitrogen and hydrogen. This method must be controlled with a silent discharge under pressure and has had very little success commercially.

V. Production of NO by causing a high temperature by means of an explosion or using catalytic agents. The method is essentially that employed by Bunsen to form water and was first used by Hansen with coke oven gases which he exploded in a bomb calorimeter to produce NO.

As to the merits of each method it is sufficient to say that the cyanamid plant at Niagra manufactured many times more than all the other processes in this country in 1918.

Object of The Work.

In my college course I had the honor and pleasure of assisting Prof. McCormack, in a minor way, in his work of separating nitrogen from the atmosphere and fixing that gas by electrical methods. 46 per cent nitrogen was manufactured, passed into an electric furnace under pressure and calcium cyanamid produced on a commercial scale. The product obtained was lower in nitrogen than that made from calcium carbide and had limited uses. The object is to extend this work to the investigation of the formation of aluminium nitride. The nitrogen content should be higher than that of the cyanamid. Only meager information is available on this subject. It is desired to establish the correct temperature, the length of time, the proper proportion of reagents and catalysts needed and the effect of various composition of gases on the formation of aluminium nitride. From these data

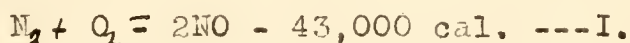
Object of The Work.

a commercial process can be worked out which in all probability, as will be shown later, will be the most suitable and cheapest method for the fixation of nitrogen.

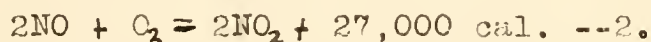
Chemistry Of The Process.

In considering the nitrogen molecule it is well to note its similarity to that of carbon. Each has two or more atoms united with a bond representing an enormous amount of energy. Nitrogen also forms ring chained bodies many of which have isomers and are optically active. The seeming great bond between the atoms themselves causes them to unite to form the inert molecular nitrogen of the atmosphere.

In the equation



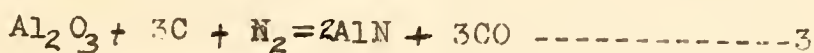
heat is absorbed the reaction being endothermic while in the equation



is also an oxidation but is exothermic. Reaction I. shows that the nitrogen atom has a tendency to combine with its self with the liberation of energy. Compounds like NO which absorb heat on formation from its elements and give up heat on decomposition are unstable.

Chemistry Of The Process.

In reaction 2, heat is given out. This shows that, after combining with other elements, the seeming great bond between the atoms having been broken, the nitrogen molecule will readily unite with other substances to form stable compounds. Therefore in all fixation processes with solid materials some catalytic agent, as finely divided iron, or an oxide must be used. The oxide has no influence on the final reaction but causes a larger yield of the product desired. It was found that using only the materials of the reaction



That no appreciable amounts of aluminum nitride was formed. Therefore the exact amount of iron oxide necessary is an important factor.

Mr. Wilber found this ratio to be $\frac{1}{2}$ to 1 % of the amount of aluminium oxide present.

The velocity of the reaction was worked out by Prof. McCormack at different temperatures

Chemistry Of The Process.

and was found to be almost instantaneous between 1700 and 1800. All results show that the reaction must be subject to accurate temperature measurements, the partial pressures must be controlled and definite zones of reaction maintained. Now there are three substances in the solid state, two in the gaseous in equation 3. The partial pressures of the solids will be their sublimation pressures, which are practically zero. We have only to deal with the nitrogen and the carbon monoxide. The partial pressures of the gases are lowered by mixing and can be controlled by allowing the CO to pass out the system burning at the back of the furnace. Without a constant agitation of materials or removing the CO, equilibrium would be produced by the solid forming a coating of compound or by the pressure of the gas generated. The reversibility of reaction 3. demonstrat-

Chemistry Of The Process.

ed by Prof.Knox in his work on fixation. He showed that when the CO was above a certain amount , the reaction took place in the opposite direction.Following the precautions given above,we should obtain a manufactured product averaging atleast 30% nitrogen.

Description Of A Fixation Process.

A method was worked in the industrial laboratory of the Armour Institute of Technology for separating nitrogen from the atmosphere by a direct combustion of oxygen and dissolving out the carbon dioxide by lime leaving 96 per cent nitrogen.

The combustion was carried on in a large brick chamber by burning crude petroleum with super heated steam by means of an oil burner. (See Plate I, AI & II $\frac{1}{2}$, O) Pg.s I4 & I8. After combustion, the gas contained only 2 per cent oxygen. Excessive heat is developed in the combustion chambers and could be utilized by boilers properly installed so as not to interfere with the primary aim of the operation. (Plate II C & D) A roaster could also be added to the furnace for drying the ore and alumina to be used in fixation. (See Plate II $\frac{1}{2}$ B). If the oil proved too expensive coal dust with a mechanical stoker could be substituted in this furnace. The

NITROGEN SEPARATION PLANT



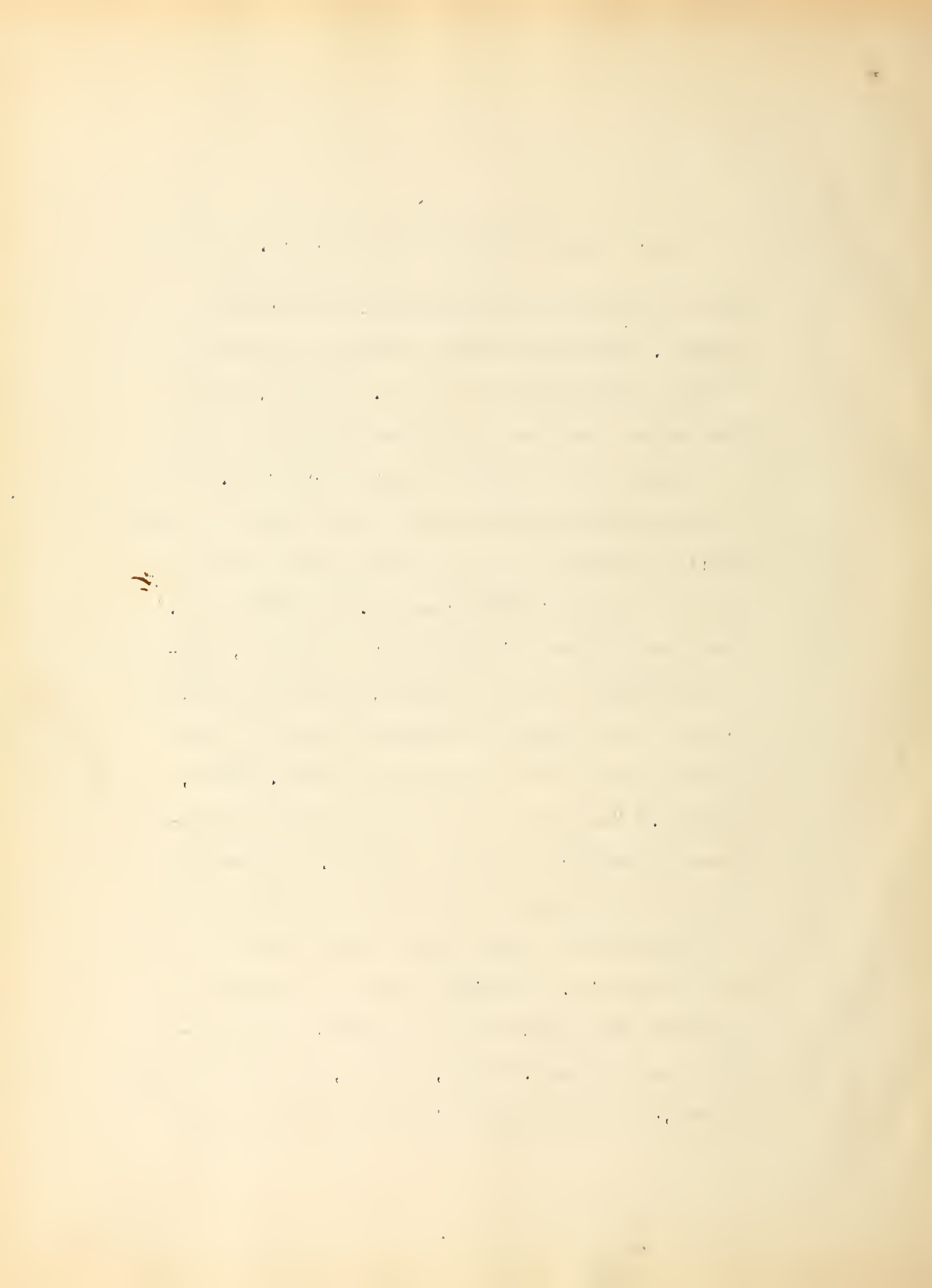
- A. COMBUSTION CHAMBER
- 1. CRUDE OIL BURNER
- B. GAS WASHER
- 1&2. WATER SPRAYS
- 3. THERMOMETER
- C. BLOWER
- D. CO₂ ABSORPTION GAS
- 1. SLIDING REMOVABLE SHELL
- 2. LUMPS OF CAUSTIC LIME
- 3. VALVE FOR TEST GAS
- E. GAS TANK
- 1&2. VALVES
- F. PRESSURE OIL TANK
- 1&1. VALVES

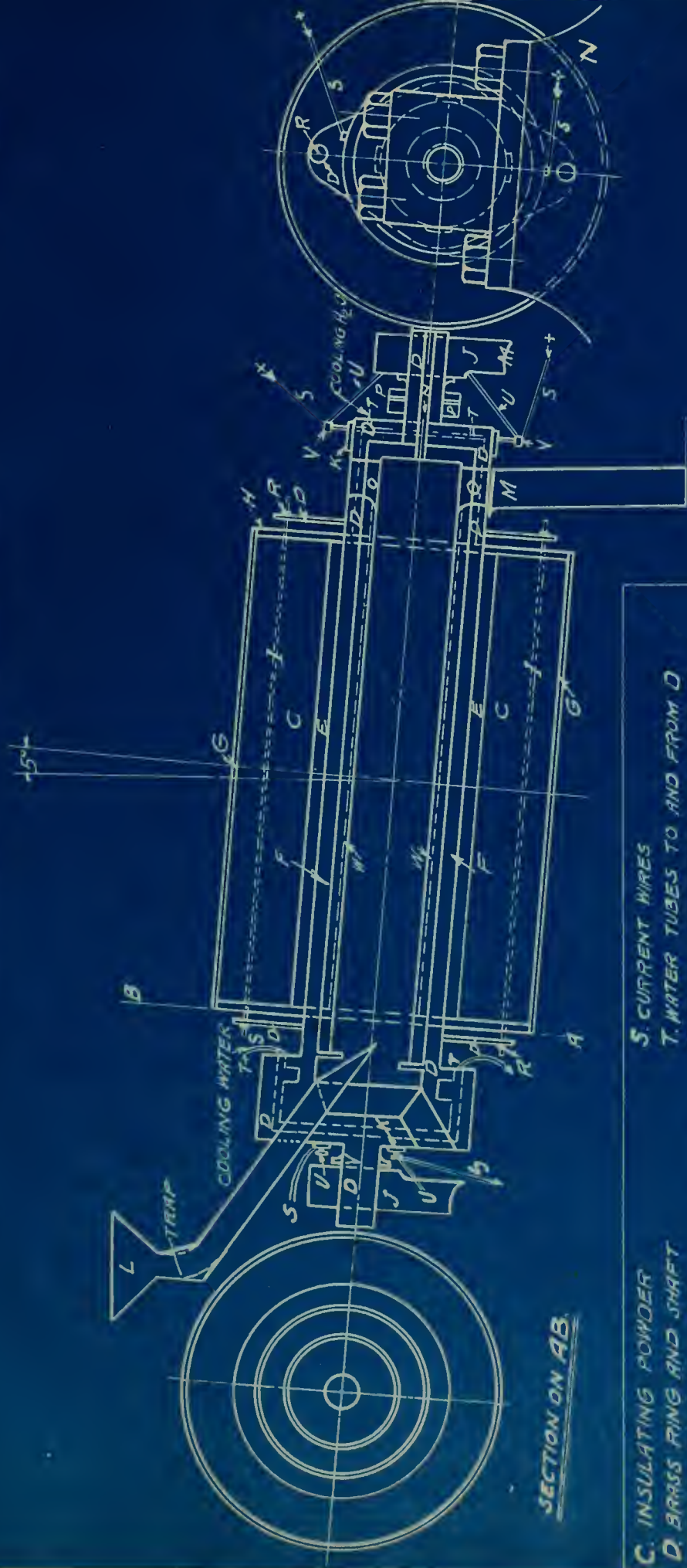
SCALE: 1/4" IN = 1 FT

FIXATION PLANT
INDUSTRIAL CHEM. LAB.
ARMOUR INST. OF TECHNOLOGY

Description Of A Fixation Process.

gas is drawn by a fan from the furnace to a washer, that contains many shelves over which trickle thin sprays of water. (See B, Plate I) The water from the gas washers could be used for boiler feed thereby saving much heat. The gas passes from the washers thru a suction fan that is regulated to give the proper amount of air to the combustion chamber. (See C Plate I.) The fan C drives the gas to the drier D, containing many sliding shelves, easily removed, of caustic lime where the carbon dioxide is dissolved out to less than two per cent. (See D, Plate I.) The gas is sent to the electric furnace or collected until required. The designers of this method believe it to be the cheapest commercial process as it will give 96 to 98 % nitrogen. The Claude, Joule or Thompson methods for separation of gases by liquefaction may be used. These, however, require a large plant, a big equipment of expensive machinery





SECTION ON AB.

- C. INSULATING POWDER
- D. BRASS RING AND SHAFT
- E. CARBORUNDUM TUBE
- F. CARBON RINGS FOR CURRENT FROM D
- G. WROUGHT IRON TUBE ENCLOSING FURNACE
- H. HARD INSULATED PLATE BOLTED TO G
- I. THE RODS BY WHICH D IS TIGHTENED TO F
- J. JOURNAL SUPPORTING FURNACE
- K. BRUSHES GIVING SLIDING CONTACT D
- L. PIPE FOR CHARGING FURNACE
- M. TUBE TO TAKE DISCHARGED AIN
- N. JOURNAL STAND
- O. VENTS IN D FOR DISCHARGING AIN
- P. PULLEY TO ROTATE FURNACE
- R. BOLTS TO TIGHTEN OR LOOSE PLATES E AND
- S. CURRENT WIRES
- T. WATER TUBES TO AND FROM D
- V. RINGS SUPPORTING BRUSHES K
- U. BRUSH RING SUPPORTS
- W. TUBE MADE OF COMPRESSED AIN AND CARBON USED TO CARRY ORE
- D'. CAST IRON PLATE BOLTED TO D
- FURNACE SLANT 5°

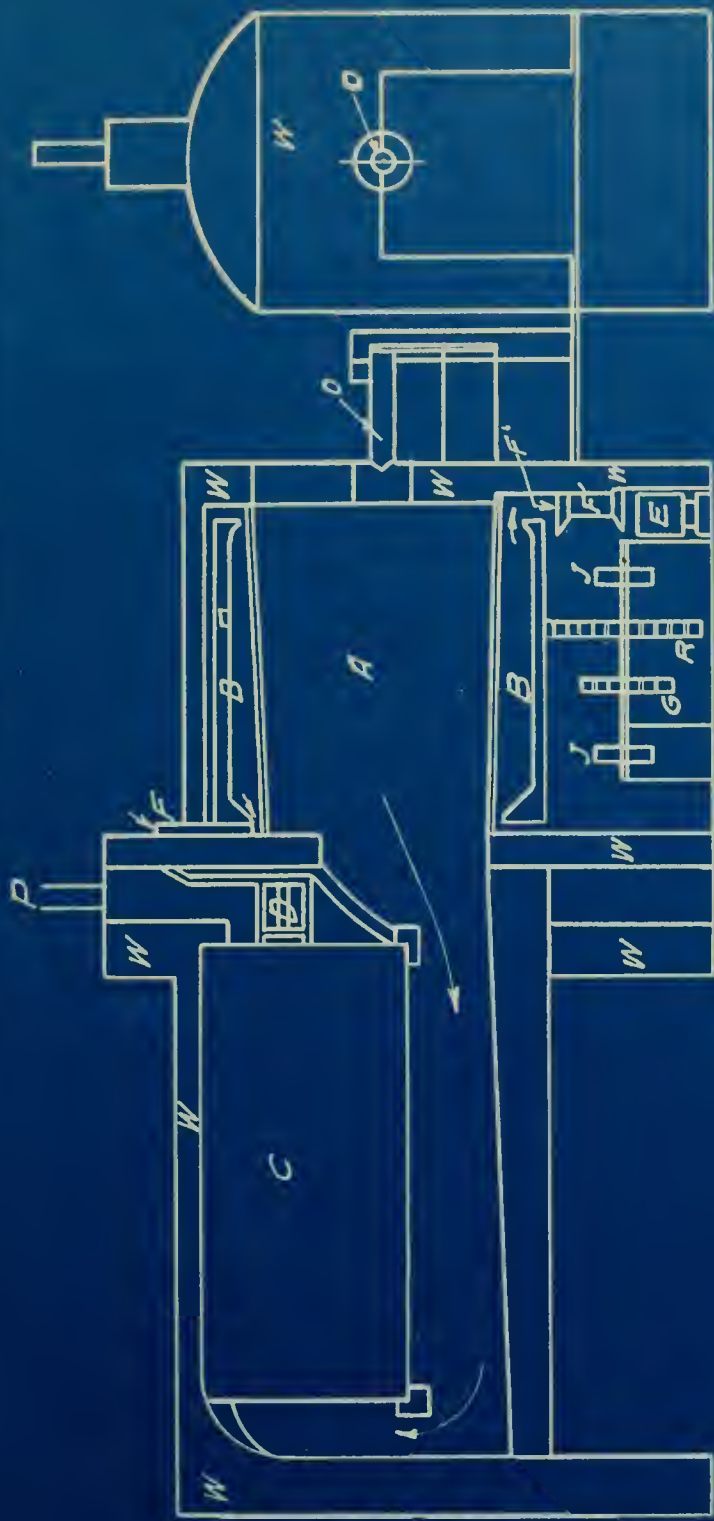
SCALE: 1/2 IN = 1 FT.

Description Of A Fixation Process.

and consume the total energy input, but give a purer gas that will make a final fixed body with a larger percentage of nitrogen.

The fixation is made in the resistance furnace that will give from 1500 to 1800 degrees. The materials were put in a carbon boat in the furnace and pure nitrogen and then other gases passed over them. This method gave yields with low results. A method of revolving the charge was then devised to give better results. A design of an electric furnace to continuously produce aluminium nitride is shown on Plate II. A method for preheating the charge with the CO escaping from the furnace should be worked out and attached to the system.

Only a very low priced plant using few attendants can be operated to manufacture nitrogen compounds and market them at the same price as those made from Chile nitre and by-product ammonia.



- A. COMBUSTION CHAMBER
 - B. DUCT FOR ORE ROASTING
 - C. BOILER FOR UTILIZING HEAT IN NGAS
 - D. SUPER HEATER
 - E. CAR FOR ROASTED ORE
 - F. ORE INLET
 - F' ORE OUTLET
 - G. POWER GEAR
 - R. RACK & PINION FOR OPERATING DRUM
 - J. JOURNAL FOR GEAR SHAFT
 - O. OIL BURNER
 - P. NGAS PIPE TO WASHER
 - W. CONCRETE WALLS OF FURNACE
- SCALE: $\frac{3"}{1"} = 1 \text{ FT.}$

Data and Results.

Charge I. total weight	--	--	1,000	gms.
" Carbon	--	--	400	"
" Bauxite	--	--	600	"
Charge I. Al_2O_3	-	--	42.34	%
Fe_2O_3	-	--	12.00	"
Si O_2	-	--	5.80	"
Carbon & moisture	-		40.00	"

Run I (a), Using pure nitrogen on charge I.

N in fixed body average of 4 heats 14.50 %

Run I.(b) Air preheated on charge I.

N fixed average of two heats -- 1.15 %

Run II. (Charge two was made on the basis of Mr Wilber's results.)

charge II, total weight	--	--	1,000	gms.
" Charge I	--	--	83	"
Carbon	--	--	366	"
Al_2O_3	--	--	551	"
Charge II Al_2O_3	--	--	58.50	%
Fe_2O_3	--	--	1.00	%
Si O_2	--	--	.40	"
Carbon	--	--	40.00	"

Data and Results.

Ratio of Fe_2O_3 to Al_2O_3 $\frac{9.96}{586} = 1.74 \%$

Run II (a) Charge II pure nitrogen

N fixed average of two heats -- 20.32 %

Run II (b) producer gas on Charge II

N fixed -- -- 12.50 %

" (c) Plant gas (96% N, 2% CO_2 , 2% O_2)

N fixed -- -- 17.50 %

Charge III. Total weight - -- 100 Gms;

" charge I -- -- 5 "

" Al_2O_3 -- -- 58 "

Carbon -- -- 37 "

% Charge III Al_2O_3 -- -- 60.00 %

Fe_2O_3 -- -- .60 "

Si O_2 -- -- .04 "

Carbon - -- 39.00 "

Ratio of Fe_2O_3 to $\text{Al}_2\text{O}_3 = \frac{.60}{60} = 1.00 \%$

Run III pure N. Charge III.

% N fixed average of 2 heats 17.40 %

" (b) Plant gas on Charge III.

N fixed 12.50 %

Data and Results.

Run III Producer on charge III

N fixed -- -- -- 6.00 %

These results were obtained by placing the charge in a carbon boat. It was decided that a coating was formed on top of the charge keeping the lower part from the nitrogen. A method was devised for rotating the carbon tube containing the charge.

Air as a successful agent in these experiments was abandoned after many trials. Pure nitrogen gives the most satisfactory results. plant gas gives fairly good products and is made cheaper than pure nitrogen could be used advantageously. The producer gas used contained 20 to 30 % CO, $2\frac{1}{2}$ to 4% CO₂, 10% O, and 57 to 70% N. The data show low percentages with this gas. With large amounts of CO and Oxygen however no catalytic action can take place. In practice 14 to 18% nitrogen is obtained by using producer gas. With pure nitrogen and the proper handling of the charge a fixed body containing 20 to 30 %

Data and Results.

could be made. The experiments of Tuccer and Read show that when selected portions of the nitride are taken much higher results are obtained. (See Bib. ref. I)

Summary:

Charge, 12% Fe_2O_3 , N gas, N fixed	-----13.5 to 16%
" " " Pl. gas "	11%
" " " Air "	1.5%

Charge, 1 to 2% Fe_2O_3 , N gas	N fixed 17.5 to 20%
" " " Pl. " " "	12.5%
" " " PrO_3 " " "	6.0%

Special charge in a rotating tube, dust from
aluminium smelter.

" 1 % Fe_2O_3 , N gas, N fixed --

Economics of Manufacture.

If the nitrogen fixation is made by burning coal or petroleum or from producer gas and the sensible heat developed used to preheat the nitrogen and to give heat to make power for the plant, then the electric power would probably be 10 Kw. Hrs. per kilogram of nitrogen manufactured. Using current on the off peak loads of the electric plant or working the furnace at nights would reduce the cost of power to $\frac{1}{2}\%$ per Kw. Hr. The power will require $2\frac{1}{2}\%$ for every pound of nitrogen made. The price of nitrogen is quoted from the market list on Chili nitrate, at present selling for \$4.07 $\frac{1}{2}$ per hundred pounds and containing 15% nitrogen. The price of nitrogen therefore would be from 13 to 15¢ per pound. The other factors involved in production besides electric power are materials and labor. A fixation plant must own its coal mines, lime and phosphate rock deposits and be located near them as the principal manu-

Economics of Manufacture.

factured article would be fertilizer, \$75,000-000 worth having been sold east of the Mississippi River in 1918. Allowing $7\frac{1}{2}\%$ for labor and transportation to the factory, a margin of 3 to 5% a pound is left for profits and interest in a fixation plant making aluminium nitride. The nitrogen can be extracted by water under pressure and is liberated as ammonia. A good selling fertilizer must contain nitrates phosphates and potassium salts. The Chemical Engineer Vol. 21 says that Potassium salts can be made from sea weeds in the West Indies for \$38.00 per ton.

A 500,000 horse-power plant for nitrogen fixation has been located on the Tennessee River in the heart of the limestone, coal and phosphate rock region. There is no reason why a plant so favorably located could not manufacture nitrogen products that could compete with the prevailing prices from other sources.

Comparison With Other Methods.

L.L. Summers E.E. gives the following costs:

Direct oxidizing of atmospheric nitrogen 5%
efficiency yield at 550 KC. per Kw. year re-
quires per Kg. -- -- -- -- 65.00 Kw. Hr.

Cyanamid process 60% efficiency in carbide 1%
loss in heater to combine with N requires per
Kg.ofN -- -- -- -- -- - 16.6 Kw. Hr.

Catalytic methods for combining N and H to form
ammonia requires per Kg.of N -- - 1.5 Kw. Hr.
and also preparation of the gases,refrigeration
and compression to 200 atmospheres.

AlN using sensible heat from nitrogen manufac-
ture to raise the products to the temperature
of reaction requires per Kg. of N -10.0 Kw. Hr.
More nitrogen is produced by the cyanamid pro-
cess than all the others at present. The pro-
duct contains 17 % nitrogen. The nitride method
as shown will give a fixed bodywith a larger
per cent nitrogen at a lower cost for power.
The power and preparation costs of the other
methods leave no comparisons to be made.

Comparison With Other Methods.

In conclusion from the summary and comparisons it may be said that the aluminium nitride process can fixate cheaper and give a product with a larger **per** cent nitrogen than any other method of to-day.



Appendix.

To Prof. McCormack I extend my sincere thanks for whatever merit there may be in this work and for his untiring patience in aiding me. To the rest of the faculty I am deeply grateful for the knowlege that lifts me above the ordinary mind.

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